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Many-body dispersion effects on the binding of TCNQ and F4-TCNQ with graphene

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ABSTRACT

Predictive modeling and understanding of binding of organic molecule-decorated graphene is an essential prerequisite for tuning their electronic and magnetic properties. Many-body dispersion (MBD) interactions are known to contribute significantly to the binding of condensed matters, but the role of MBD energy in self-assembled organic monolayers on epitaxial graphene remains largely unexplored. Here, by using the state-of-the-art DFT + MBD method, we for the first time investigate model π-π adsorption systems that are composed of two typical acceptor molecules, TCNQ and F4-TCNQ, and graphene sheets. The computed binding energies from the DFT + MBD method are consistently smaller than those from the pairwise-based van der Waals (vdW) inclusive method, such as DFT + vdW, due to the accurate capture of both electrodynamic screening and many-body effects in the former case. Notably, many-body effects contribute more to the low-coverage adsorption systems than they do when the substrate is highly covered by the adsorbates. This somewhat counter-intuitive result is attributed to the fact that each molecule contributes less to the polarization of the hybrid interface at high coverage.

1. Introduction

Self-assembly of organic molecules on two-dimensional materials, in particular graphene sheets, is a rapid and reliable scheme in nanotechnology to design functional interfaces and electronic nanodevices with tunable properties [1–6]. The architecture of self-assembled monolayers (SAM) is dominated by non-covalent interactions, such as van der Waals (vdW) forces, hydrogen bonds, and halogen bonds [7,8]. The hydrogen and halogen bonds, as stabilizing interactions in SAMs, have been intensively studied for a long time. However, recently, it was realized that vdW forces can largely determine the preferred adsorption site, and define the growth of molecular films in dynamics for systems with weak intermolecular interactions [9].

Density-functional theory (DFT) is the most feasible approach to treat complex interfaces at the quantum level. Nevertheless, the absence of long-range dispersion in exchange-correlations often leads to incorrect predictions for a given system [10–13]. In this context, a number of vdW-inclusive DFT methods have been developed, such as DFT-D [14,15], DFT + vdW [16], Becke-Johnson model [17], and vdW-DF [18–20]. A general feature of these approaches is their treatment of long-range dispersion in a pairwise way, neglecting the effect of collective excitations in the system [21]. Although such collective effects are dispensable in gas phase, particularly for small molecules, they become significant for condensed matters due to the strong screening of surroundings [22].

To go beyond the pairwise correction scheme, Tkatchenko's group has recently developed a promising method termed as many-body dispersion (MBD) [23]. By construction, the long-range correlation of atoms in this approach is determined by the coupling of quantum harmonic oscillators. Compared with pairwise-based approaches, the MBD method can properly treat many-body contributions and short-range screening effects, and obtain more accurate vdW C_6 coefficients and polarizabilities [24]. The DFT + MBD method has been successfully applied to a variety of systems, such as supramolecular systems, molecular crystal, nanoclusters, and layered nanostructures [25–30]. A unifying aspect of these studies is the observation of greater many-body effects for more condensed systems. As exemplified by silicon nanoclusters, accurate C_6 coefficients can be obtained for small molecule (SiH_4) by the pairwise DFT + vdW method [23]. However, the error in C_6 increases dramatically for larger systems, for example, by 27% for $Si_{172}H_{120}$ and 68% for Si bulk. In contrast, the MBD method considering long-

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range screening effects is well consistent with the experiment, with an error of 8% for Si bulk. In this context, one may naturally assume that many-body effects would contribute more to the high-coverage adsorption systems, such as highly-ordered self-assembled system, than they do when the surface is sparsely covered with adsorbates.

To assess the validity of the assumption, in this contribution we choose to study TCNQ and F4-TCNQ on graphene sheets – two prototype graphene-based self-assembly systems that have the potential application in electrodes, magnetics, and diodes [31]. A number of recent experimental and theoretical studies have already focused on the TCNQ/graphene and F4-TCNQ/graphene systems. Using spin-polarized scanning tunnelling microscopy, Garnica *et al.* [32] observed long-range magnetic order for self-assembly TCNQ layer adsorbed on epitaxial graphene grown on Ru(0001). Hsu *et al.* [33] fabricated an anode structure composed of two TCNQ layers sandwiched by three graphene layers, which exhibits relatively higher power conversion efficiency. In the aspect of theoretical calculations, Oliveira *et al.* [34] employed the pairwise DFT + vdW method and studied the preferable structure and stability of TCNQ and F4-TCNQ on graphene. However, to the best of our knowledge, prior computational studies concerning molecular self-assembly on graphene were carried out using pairwise models [34–36]. Herein, for the first time, we apply the MBD method to study the interactions of organic molecules with graphene sheets, and demonstrate profound MBD effects in such hybrid interfaces. Notably, the polarization in dispersion interactions exhibits anisotropic characteristic, which leads to stronger (weaker) screening effects along the perpendicular (parallel) direction. Somewhat contrary to intuition, we find that many-body contributions actually decrease with increasing adsorption coverage.

2. Methods

DFT calculations were performed in the numeric atom-centered basis set all-electron Fritz Haber Institute ab initio molecular simulations (FHI-aims) package [37,38]. The vdW interactions were calculated using the state-of-the-art MBD method, coupled with the generalized gradient approximation (GGA), in the form proposed by Perdew, Burke, and Ernzerhof (PBE) [39]. For comparison, we utilized the PBE + vdW method to account for the pairwise vdW interactions. The hybrid Heyd-Scuseria-Ernzerhof (HSE) functional [40] was employed to investigate the effect of electronic self-interaction, which has an accurate treatment of screened exchange in the underlying functional. The “tight” settings including the “tier2” standard basis set in the FHI-aims code were used for H, C, N, and F. All atomic positions were relaxed until the maximal force on each atom was smaller than 0.02 eV/Å. For all computations, the convergence criteria of 10^{-4} electrons per unit volume for the charge density and 10^{-5} eV for the total energy of the system were utilized. We performed spin-polarized calculations for TCNQ on graphene with various coverage and found that the magnetic moment of all studied systems is zero (supporting information, Fig. S5). The Brillouin zone was sampled according to the Monkhorst-Pack method [41], where a 5 × 5 × 1 mesh was used for the single molecule and pattern calculations. And a 3 × 5 × 1 mesh was used for the calculations at coverage of 0.5, 0.75, 1.25, 1.5, 1.75, and 2 ML. Different slabs were separated by 100 Å of vacuum to eliminate the interaction between periodic images.

3. Results and discussions

3.1. MBD effects for single TCNQ and F4-TCNQ on graphene

We started by exploring the potential-energy surface (PES) and related adsorption configurations for a single TCNQ and F4-TCNQ adsorbed on graphene. To determine the optimal conformation, we performed geometry optimizations for six high-symmetry adsorption sites by PBE + vdW, which are termed as “bridge-x, bridge-y, hollow-x, hollow-y, top-x, and top-y”, see Fig. 1(a). After geometry relaxations, we calculated adsorption energies by the PBE + vdW and PBE + MBD methods to explore the contributions of MBD effects. The adsorption energies, E_{ads}, were determined by

$$E_{\mathrm{ads}} = \left[E_{\mathrm{sys}} - E_{\mathrm{gra}} - nE_{\mathrm{mol}}\right]/n \tag{1}$$

where E_{sys}, E_{gra}, and E_{mol} denote the total energies of the adsorption system, the graphene layer, and the isolated molecule, respectively. And n is the number of molecules in a unit cell.

Fig. 1(b) and (c) present the adsorption energies for a single TCNQ and F4-TCNQ on graphene, from which TCNQ preferably adsorbs at the bridge-y site, with an adsorption energy of −1.53 eV

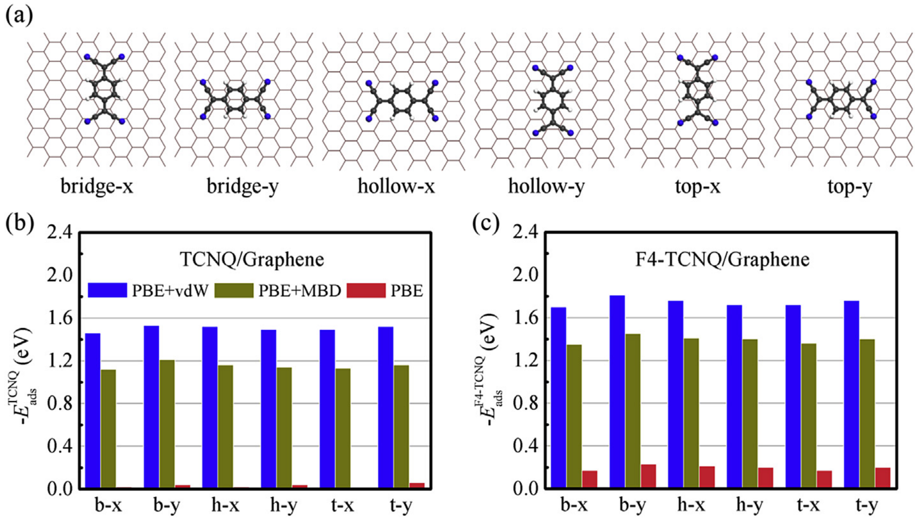

Fig. 1. (a) Six adsorption sites of TCNQ and F4-TCNQ on graphene, which are represented by a TCNQ molecule on graphene in a cubic cell with the size of $12a_c \times 6\sqrt{3}a_c$, where a_c is the length of C–C bond. (b) and (c) Adsorption energies of a single TCNQ and F4-TCNQ molecule on graphene computed from different methods. (A colour version of this figure can be viewed online.)